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The study of magnetic anisotropy and susceptibility of ruthenium acetylacetonate

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Magnetic anisotropy and susceptibility of Ru^{3+} ion in ruthenium acetylacetonate crystal in the temperature range from 300°K to 90°K are reported in this communication. Both the results show marked deviation from the Curie law. The anisotropy is very large varying from 60% to 125% of the mean susceptibility in the above temperature range. The effective moment is nearly 1.9 BM near room temperature. All these results clearly indicate that the usual weak field scheme completely fails in this case. A strong ligand field treatment must have to be invoked to interpret the present findings in terms of anisotropic ligand field theory. In particular, the present anisotropy data together with the mean susceptibility results will be most fruitful for accurate evaluation of anisotropic ligand field and covalency parameters and also for obtaining a knowledge about the expected variation of anisotropic part of the ligand field with temperature as observed in the salts so far investigated in our laboratory.

Introduction

Very little work on the magnetic behaviour of single crystals of paramagnetic complexes belonging to the palladium (4d) and platinum (5d) groups of elements has yet been done. Moreover, the present theories were found to be inadequate to explain the observed experimental data. The complexes of palladium and platinum groups of elements differ from those of the first transition (3d) elements mainly because of four factors—(*a*) stronger crystal field (*b*) stronger spin-orbit coupling (*c*) interelectronic repulsion comparable to spin-orbit coupling (*d*) larger overlap of charge clouds of 4d or 5d electrons with the ligands. A study of magnetic anisotropy as well as mean susceptibility and their variations with temperature should provide useful informations on the relative contributions of the factors involved and enable us to extend the ligand field theory in these cases also.

The case of ruthenium acetylacetonate belonging to the palladium group is interesting in the sense that electronic configuration of the ground state of the free ion Ru^{3+} being $4d^5\ {}^6S_{5/2}$ in the Russel-Saunders Scheme, a weak field treatment would lead to a very feeble magnetic anisotropy of the ion, the spin moment would correspond to an effective Bohr magneton 5.9 and the mean susceptibility should follow a Curie law very accurately. Figgis *et al* (1966) have measured the mean susceptibility indicating a value of effective moment 1.9 BM at room temperature. There is also appreciable deviation from the Curie law. Weak field procedure therefore is

obviously not apt in this case. Figgis *et al* (1966) from their above data have evaluated the axial field splitting Δ of the lowest degenerate state, a triplet under strong field scheme. Evaluation of Δ from mean susceptibility alone is not considered to be very accurate since unlike the magnetic anisotropy the mean susceptibility is not very sensitive to the axial field. Moreover, the axial field may change appreciably with temperature, which will be hard to detect from mean sueceptibility alone, so that the above mentioned calculation of Δ is not very significant. Again the calculation of the covalency factor (Figgis *et al* 1966) from mean susceptibility does not take into account the anisotropy in the delocalization of the ligand and central ion electrons. All these informations can be obtained much more precisely from anisotropy and mean susceptibility results when considered together.

In view of these, a detailed experimental investigation of the magnetic anisotropy and susceptibility of ruthenium acetylacetonate has been undertaken and the experimental values are reported in this communication.

Preparation of the crystal

Ruthenium acetylacetonate was prepared by treating aqueous ruthenium trichloride and acetylacetone solution with potassium bicarbonate solution and than refluxing the mixture (Wilkinson 1952, Hartmann & Buschbeck 1957, Grobelny *et al* 1966). The red precipitate of the compound was washed repeatedly, filtered and dried. The single crystals were grown from benzene solution by very slow evaporation.

Structural data

No detailed crystal structure has yet been investigated. Jarrett (1957) has reported preliminary measurements on aluminium-, chromium-, cobalt-, and ruthenium acetylacetonates and found them to be isomorphous. Dingle (1965) from a study of external morphology and X-ray powder pattetn has also substantiated the isomorphism and concluded that they should belong to the monoclinic space group C^5_{2h} with four molecules in the unit cell. Three acetylacetonate groups surround the metal ion to form an octahedron of three pairs of chelating oxygen atoms. Thus it may be presumed from the stereo-chemical considerations that the crystalline field has a trigonal symmetry analogous to some of the other isomorphous compounds as observed by Singer (1955).

Experimental Technique

(*a*) *Mean susceptibility*

The mean susceptibility was measured with the help of a very sensitive Curie type balance but of robust construction designed by Bose *et al* (1963). Suspension of the balance beam was of moderately thick phosphor-bronze

strip and the deflectional sensitivity was made very high by using a balanced pair of photo-electric cells connected across a galvanometer and actuated by a light apot reflected from a mirror at the centre of the balance beam. The sample is suspended vertically from one arm of the beam in the central part of a Sucksmith type of inhomogeneous horizontal magnetic field with a small gradient at right angles to the field in the same plane. The translational magnetic force on the sample is balanced electrodynamically by the force exerted on a small current bearing coil attached rigidly to the other arm of the balance beam and placed in the field of a small permanent magnet.

The sample hangs freely within the experimental chamber of a new type of liquid oxygen cryostat (Bose *et al* 1963) placed between the poles of the electromagnet in which any desired temperature between 400°K to 65°K may be reached and kept automatically constant within 0.01°K. The temperature at the crystal is measured with a calibrated Cu-constantan thermocouple. The mass susceptibility of the sample at room temperature is calculated from the expression,

$$\chi = \frac{i}{i_s}\left(\chi_s - \frac{k_a}{\rho_s}\right)\frac{m_s}{m} + \frac{k_a}{\rho}$$

in which χ, i, m and ρ are the mass susceptibility, balancing electric current, mass and density of the sample ; χ_s, i_s, m_s and ρ_s are those of the standard chromium potassium alum, k_a being the volume susceptibility of the surrounding air.

Although the mean susceptibility results have already been reported by Figgis *et al* (1966) we have measured it again with our very accurate susceptibility balance and the cryostatic device mentioned earlier. The measurements are shown graphically side by side (figure 1) with those given Figgis *et al* (1966) showing an appreciable difference except at very low temperatures.

(*b*) *Anisotropy*

The magnetic anisotropy is measured by the null deflection method developed here (Dutta 1956). The crystal specimen is attached to the lower end of a thin glass rod with a known plane or axis horizontal or vertical with the help of a two-circle goniometer. The glass rod in turn is suspended from an accutate vernier torsion head reading to 0.1°, by means of a fine quartz fibre. The image of an illuminated scale, from one or the other of a hexagonal set of vertical mirrors attached to the upper end of the glass rod, can alawys be observed as the crystal is rotated. The crystal is suspended inside the experimental chamber of a liquid oxygen cryostat placed between the poles of a strong electromagnet.

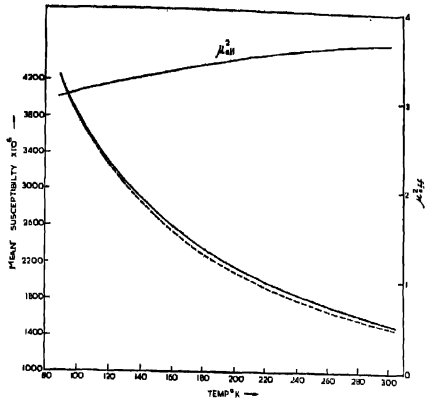

Figure 1. Showing curves for μ_{eff}^2 vs. T (right-hand scale) and $\bar{\chi}$ *vs* T (left-hand scale). The dotted line is due to Figgis *et al* (1966)

The position of the crystal for zero couple in the magnetic field, corresponding to setting of the crystal with its maximum susceptibility direction in the horizontal plane along the lines of forces, was obtained by rotating the torsion head till the twist in the fibre was nil. The crystal is then turned through in the absence of the field to the maximum couple position i. e. at 45° to the initial setting position. The magnetic field is now switched on again, which causes the crystal to rotate, towards zero setting position and it is brought back to the 45° position by rotating the torsion head. The gram-molecular anisotropy $\Delta\chi$ in the horizontal plane of the crystal is given by

$$\Delta\chi = \frac{2\alpha MC}{180mH^2}$$

where α is the angle through which the torsion head is rotated from 45° position. C, the torsion constant of the fibre, H, the magnetic field, M and m, the molecular weight and mass of the crystal respectively.

The constant C/H^2 is determined with the help of a standard nickel sulphate hexahydrate crystal whose anisotropy is accurately known (Dutta 1956).

For anisotropy measurement at any desired temperature in the range 300° to 90°K, the automatic gas flow-type cryostat (Bose 1947) was used. The

liquid oxygen kept in a seperate reservoir, was pumped into the cryostatic chamber, evaporated and made to flow round the experimental chamber, the control of temperature being effected partly by adjusting the flow of liquid and partly by a gas thermometer relay device. Any desired temperature can be maintained steady to better than 0.1°K and measured accurately with a calibrated Cu-constantan thermocouple.

For a monoclinic crystal the anisotropy in the horizontal plane measured, where the crystal is suspended with b axis vertical, is given by

$\Delta\chi = (\chi_1 - \chi_2)$. It is assumed as usual that one of the principal susceptibility axes, say χ_3, is along the b axis by symmetry requirements, and of the two principal susceptibilities in the (ac) plane χ_1 is greater than χ_2. Also χ_1 and χ_2 make angles of ψ and θ with c and a axes of the crystal respectively.

With a axis vertical the anisotropy is

$$\Delta\chi = \pm \{ (\chi_1 - \chi_2) \sin^2\theta - (\chi_1 - \chi_3) \}$$

and with (001) plane horizontal

$$\Delta\chi = \pm \{ (\chi_1 - \chi_2) \cos^2\theta - (\chi_1 - \chi_3) \}$$

The + ve or − ve sign is chosen according as the b axis lies along or normal to the field, in the present case the former sign is the correct one. Using the above formula the values of $(\chi_1 - \chi_2)$, $(\chi_1 - \chi_3)$ and θ are obtained at different temperatures. The value of θ can also be obtained by finding the orientation of two $h0l$ planes in the magnetic field with b axis vertical (Datta 1956).

Since from the structural data we have assumed a trigonal symmetry of the ligand complex, the principal ionic susceptibilities are $K_z = K_\parallel$ along the trigonal axis and $K_x = K_y = K_\perp$ perpendicular to this axis. Then the ionic anisotropy is calculated from the expressions

$$K_\parallel - K_\perp = 2(\chi_1 - \chi_2) - (\chi_1 - \chi_3), \text{ when } K_\parallel > K_\perp$$

$$K_\perp - K_\parallel = (\chi_1 - \chi_2) + (\chi_1 - \chi_3), \text{ when } K_\perp > K_\parallel$$

The expressions for the angle between the symmetry axes of the two magnetically inequivalent ions, one derived from the other by reflection in the (ac) plane are given in the two cases by

$$\cos 2\phi = \frac{\chi_1 - \chi_3}{K_\parallel - K_\perp}, \text{ when } K_\parallel > K_\perp$$

$$\cos 2\phi = \frac{(\chi_1 - \chi_2) - (\chi_1 - \chi_3)}{K_\perp - K_\parallel}, \text{ when } K_\perp > K_\parallel.$$

The ambiguity in the sign of $| K_{\parallel} - K_{\perp} |$ can be removed if epr values on $g_{\parallel}$ and $g_{\perp}$ are available, or in some special cases from the magnetic anisotropy data itself leading to $\cos 2\phi > 1$, or inconsistent and unreasonable fitting of the data with the theory. In our present case epr data give $g_{\parallel} = 2.82$ and $g_{\perp} = 1.52$ so that we may take $K_{\parallel} > K_{\perp}$ and used the proper formulae for calculating $K_{\parallel} - K_{\perp}$ and $\cos 2\phi$ at different temperatures. It can be mentioned that our magnetic investigation alone unambiguously shows that $K_{\parallel} > K_{\perp}$ which is supported also by the epr data. The other alternative $K_{\perp} > K_{\parallel}$ leads to an absurd value of $\cos 2\phi > 1$.

Experimental Results.

The results of principal crystalline anisotropies $\chi_1 - \chi_2$, $\chi_1 - \chi_3$ at 20° interval from smoothed out graphs are shown between 300°K and 90°K in table 1. The table includes values of θ at different temperatures and the values of ϕ and $K_{\parallel} - K_{\perp}$ calculated at these temperatures using formulae mentioned earlier are also given. The results of mean susceptibility at the same temperatures are shown in figure 1 together with those of squares of effective moments.

Table 1

T°K	$(\chi_1-\chi_2)\times 10^6$	$(\chi_3-\chi_1)\times 10^6$	θ	ϕ	$K_{\parallel} - K_{\perp}$
300	296	319.7	56.4	55°14′	911.7
280	330	357.1	56.2	55°13′	1017
260	378	406 5	56.2	55°10′	1162
240	435	449.6	56.2	54°57′	1319
220	510	497.0	56.0	54°33′	1517
200	600	562.5	56.0	54°16′	1762
180	723	650.1	56.0	53°58′	2096
160	880	767.6	56.0	53°51′	2527
140	1080	922.7	56.0	53°42′	3082
120	1317	1127	56.0	53°41′	3761
100	1623	1404	56.0	53°43′	4650
90	1820	1599	56.0	54°6′	5239

Discussions

We have seen that the electronic structure of Ru^{3+} free ion is $4d^5$ $^1S_{5/2}$. But under the strong field scheme as it appears to hold in the present

case the effect of the strong octahedral ligand field on the d-orbitals is manifested by the fact that R-S coupling is broken and the single electron d orbitals break up into a ground triplet t_{2g}, with a wide separation from the upper doublet e_g. The available electrons completely fill up two of the t_{2g} orbitals leaving one unpaired electron in the third orbital. The ground state of the system will be ${}^2T_{2g}$ $(t_{2g}{}^5)$. The Coulomb repulsion cannot split this orbital triplet. Thus the magnetism of the compound corresponds roughly to spin quantum number $S = 1/2$ (equivalent to magnetic moment $\mu = 1.73\ BM$) as is to be expected for the configuration $t_{2g}{}^5$. However the observed room temperature moment $\mu = 1.91\ BM$ is appreciably higher than the spin only value. This shows that the orbital moment has not been fully quenched as is to be expected for the case of a T_{2g} state lying lowest under the cubic field. As opposed to the weak field scheme in which case the magnetic anisotropy should be very feeble, our measurements show the magnetic anisotropy of the complex to be very high, about 60% at 300°K and it increases to 125% at 90°K. This is indeed to be expected in the case of an orbital triplet lying lowest in the cubic field stark pattern and further split up (to the order of kT) by the axial field. This large anisotropy is confirmed from *esr* measurement which shows the g factors $(g_{\parallel} = 2.82, g_{\perp} = 1.52)$ are highly anisotropic. Thus the case resembles Ti^{3+} ion under a predominant octahedral field with a small trigonal component except for conditions mentioned earlier. Perhaps an even better analogy is the case of potassium ferricyanide with some modifications as required by the said conditions.

Table 1 shows that ionic anisotropy of trivalent ruthenium in ruthenium acetylacetonate is about 60% and 125% of the mean susceptibility values at 300° and 90°K respectively. The crystalline anisotropy depends in a complicated manner on temperature, increasing by about 5 times when the temperature is reduced from 300°K to 100°K. It should be noted here the mean susceptibility increases by only 2.6 times in the same range of temperature. This shows that neither the mean value nor the anisotropy obeys the Curie law, though the deviation is less marked in the former (see graph). This is again to be expected for a triplet orbital state lying lowest.

The table shows that both θ and ϕ change very little with temperature, in the range of temperature from 300°K to 90°K they change only by 0.4° and 1°33′ respectively. However the negligible changes of θ and ϕ should not be considered as conclusive indication of absence of any orientational change of the ion. In $Cu(NH_4SeO_4)_2\ 6H_2O$ crystal (Bose *et al* 1957) although ϕ and θ are found to vary very little with temperature (about 1°), the recent epr experiments (Ghosh *et al* 1967) which offer a direct probe into the ion,

shows that the ion rotates appreciably in its own symmetry plane keeping the symmetry axis fixed. The rotation of the ion about its symmetry axis will not be reflected in the values of θ and ϕ which will therefore remain unchanged. Thus even though θ and ϕ do not change appreciably with temperature, the ion may undergo appreciable orientational changes which affect the packing of the lattice with consequent changes in the anisotropic part of the ligand field with temperature. Thus, apart from normal deviation from the Curie law we may expect further deviations from even the Curie-Weiss Law owing to thermal dependence of the ligand field.

Detailed theory for this complex will be shortly reported interpreting the above experimental results.

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